Spin-Forbidden Reactions in Transition-Metal Chemistry

Jeremy N. Harvey

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK
jeremy.harvey@bristol.ac.uk

Introduction

The material in this book, and indeed the very fact that the book exists, provide ample evidence for the growing maturity of computational organometallic chemistry. Computational methods, especially those based on *ab initio* quantum chemistry, are increasingly providing useful support and guidance to the experimental investigation of the properties of organometallic compounds. In this Chapter, I want to address a very common type of reactivity of these compounds, for which standard computational methods have not yet proved as successful, and to outline the strategies that have and will be used to tackle such systems.

After describing why there is a problem, I will briefly summarize the theoretical description of spin-forbidden reactions. It will be useful at this point to draw parallels with other types of non-adiabatic chemistry, in particular electron transfer. Then, I will review some of the typical contexts in which spin-forbidden behavior occurs in transition metal systems, to try to illustrate how widespread it is. This will be followed by a presentation of strategies used for characterizing and understanding spin forbidden reactions, based on the use of energies and gradients derived from *ab initio* electronic structure calculations. Finally, I will discuss the appropriateness of the different electronic structure methods for such work, before a concluding section, which will provide some guidelines for how best to set about the computational investigation of a spin-forbidden reaction.

Because spin changes are so widespread in transition metal chemistry, many studies have touched upon the subject in more or less detail. The focus of this Chapter will be on presenting strategies for the investigation of this chemistry, with some examples, mostly drawn from work I have myself been involved in, for illustration. I have therefore not attempted a comprehensive review of all the work in the area, and there are certainly many important studies of which I am aware, and probably many more of which I am not, which are not cited here, for which I would of course like to apologize.

The Problem

The partially filled shell of *d* electrons on the metallic center dominates the chemistry of transition metal compounds. Bare transition metal atoms have unpaired electrons in this shell, leading to high-spin configurations. In the presence of ligands, the degeneracy of the *d* orbitals is split to a greater or lesser

extent, which may lead to low-spin configurations, if the gain in energy from occupying a lower-lying orbital is large enough to compensate for the pairing energy. In many compounds, however, the *d*-orbital splitting, caused by the ligand field, is intermediate in magnitude, so that high- and low- spin configurations lie relatively close in energy. During a chemical reaction, if the ligand field changes, the ground state of the products may have a different spin state than that of the reactants. Such a reaction is referred to as *spin-forbidden*, because in the absence of spin-orbit coupling, passing from a potential energy surface of one spin to another of different spin is "forbidden" and does not happen.

There has been considerable debate in the literature concerning the effect of spin-state change on the rates of chemical reactions. Thus, one recent paper [1] raised the question, "Can Spin State Change Slow Organometallic Reactions ?" in the context of a study of CO ligand addition/elimination in a cobalt complex: (Tp' is a modified tris(pyrazolyl)borate ligand)

$$Tp'Co(CO)_2 \leftrightarrow Tp'Co(CO) + CO$$

The left-hand dicarbonyl complex is a singlet, whereas the monocarbonyl derivative is a triplet, so that the process is clearly spin-forbidden. Despite this, the authors observed the equilibrium between the two to be rapid and concluded: "It seems thus implausible that changes in spin state should slow organometallic transformations as a general rule."

As against this, there have been many observations of spin-forbidden reactions that *are* in fact slow. One example is provided by comparing the following two reactions (also CO association processes!):

$$Fe(CO)_3 + CO \rightarrow Fe(CO)_4$$

$$Fe(CO)_4 + CO \rightarrow Fe(CO)_5$$

The first of these two gas phase reactions is observed to proceed essentially at the collision rate, whereas the second is 500 times slower [2]. This difference in speed cannot be blamed on the existence of a barrier in the second case, because the rate is not appreciably changed by temperature. Instead, one can note that $Fe(CO)_3$ and $Fe(CO)_4$ have triplet ground states, whereas $Fe(CO)_5$ is a singlet, so that the first reaction is spin-allowed, whereas the second is spin-forbidden. Clearly, spin *does* play a role in this and many other cases.

In fact, such apparently contradictory observations are reconciled within the theoretical description of spin-forbidden reactions. As discussed at greater length below, such reactions can be roughly considered to require (a) that the system reach a configuration where the potential energy of the two spin-states are nearly equal, and (b) that the spin-orbit coupling between spin states should then cause the system to change spin. In cases where spin-orbit coupling is strong, requirement (b) is easily fulfilled, so that the corresponding reactions will not necessarily be slower than comparable spin-allowed ones. However, requirement (a) may lead to very slow reactions, because the potential energy surfaces (PESs) of the two states may be so different that they only cross at rather high energy, leading to a substantial activation barrier. The speed of the reaction will thus depend on the strength of the spin-orbit coupling, and on where the relevant PESs approach each other.

The problem mentioned in the title of this section is that locating the regions where PESs of the reactant and product spin-states approach one another is difficult within computational *ab initio* quantum chemistry. Also, the way in which the two factors mentioned above combine to determine the rates of spin-forbidden reactions has sometimes been ill-appreciated. Taken together, these facts have meant that computational studies have not contributed to understanding the *mechanistic role* of spin changes in quite the same way that they have helped to clarify the mechanisms of many other reactions of transition-metal systems.

Solving the electronic Schrödinger equation for anything but the simplest systems is an extremely complex numerical problem, which relies heavily on the use of approximations. One of the most important of these is already present in the choice of the Hamiltonian, which in almost all computational studies is taken to include only the kinetic energy and Coulombic charge interaction terms, because these are usually quantitatively the most important [3].

$$H_{elec} = \sum_{i}^{n_{el}} \frac{-\nabla_i^2}{2} + \sum_{i}^{n_{el}} \sum_{j>i}^{n_{el}} \frac{1}{r_{ij}} + \sum_{a}^{N_{nucl}} \sum_{i}^{n_{el}} \frac{Z_a}{r_{ia}}$$

Inclusion of Pauli's exclusion principle leads to the standard methods of *ab initio* computational chemistry. Within these methods, molecular systems containing the same nuclei and the same number of electrons, but having a different total electronic spin, can roughly speaking be said to be *different systems*. Thus, matrix elements of the Hamiltonian between Slater determinants corresponding to different spin states will all be zero, and they will not interact or mix at all. The wavefunctions obtained will be pure spin states.†

This will be true even in the vicinity of a crossing between PESs corresponding to different spin states. This should not in fact be so, because small (or not so small !) terms have been omitted from the Hamiltonian [4], and these terms lead to coupling and therefore mixing of different spin-states in the wavefunction. The most important of these terms, for our purposes, is the spin-orbit coupling. Whilst it is possible to include this term in *ab initio* computations [5,6], this leads to significant computational difficulties, so that it is not realistic to do so in general computations of PESs. For example, analytical gradients are not available for spin-orbit coupled methods. These gradients play a very important role in characterizing the mechanisms of adiabatic reactions, by facilitating the location of saddle-points or transition states on the corresponding adiabatic PESs. The unavailability of gradients makes it nearly impossible at present to locate stationary points on spin-mixed PESs. Because of the computational difficulties, advances in this area do not appear to be forthcoming, so that for the foreseeable future, *ab initio* calculations, at least for large systems, will be restricted to single spin-state PESs. Because the regions where one PES crosses another have no special features if one considers each PES individually, locating these regions is not straightforward. This is the fundamental difficulty that impedes the exploration of spin-forbidden reaction mechanisms in transition-metal systems.

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† *Unrestricted* wavefunction methods (see ref. [3]) lead to mixed spin states, but this is of no help in the present context.

Overview of theory

Spin-forbidden reactions are a subset of the broader class of *electronically non-adiabatic* processes, which involve more than one PES. The fundamental theory of how such processes occur is well understood [7,8,9], and a very large amount of research is being performed with the aim of elucidating more details in all the areas of non-adiabatic chemistry. It is not possible to present this work here, so I will instead provide an outline of the most important theoretical insights in the context of spin-forbidden reactions, as well as outlining the similarities with other non-adiabatic processes occurring in transition-metal systems.

In simple terms, one may describe chemistry using a semi-classical model involving motion of the system through phase space on several coupled potential energy surfaces (PESs). The potential energy is the electronic energy of the system at a given nuclear configuration. The following discussion refers to the schematic PESs shown in Figure 1:

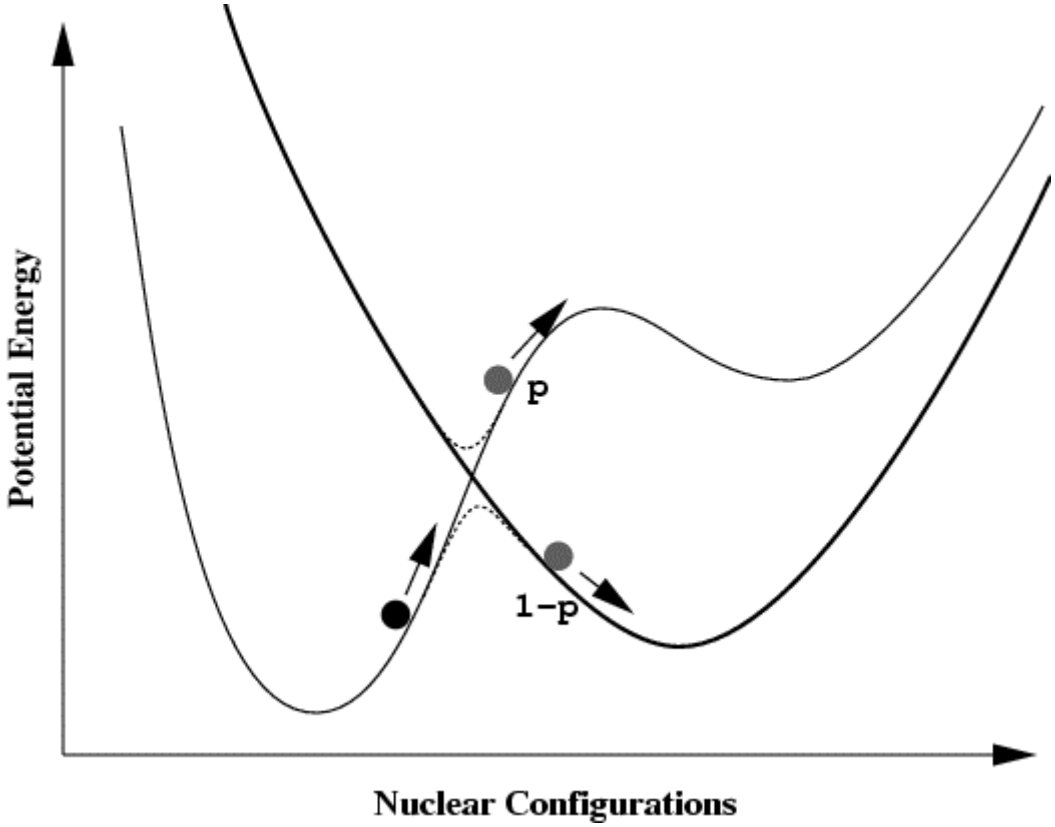

Figure 1. Schematic PESs, with the diabatic curves, corresponding to well defined spin states, shown as solid lines, and the adiabatic curves in dotted lines. The hopping event of a classical particle as it moves through the crossing region is schematically illustrated.

The PESs (solid lines) are shown here as *crossing* each other. If the potential energy is obtained by diagonalizing the complete electronic Hamiltonian of the system, including the spin-orbit coupling terms, PESs tend *not* to cross, although they may do so in regions called *conical intersections* which do not directly concern us here [8]. As mentioned above, though, most *ab initio* calculations do not use the full electronic

Hamiltonian, using only the Coulomb and kinetic terms, and within this simplified Hamiltonian, PESs corresponding to different spin states do not mix at all and may therefore cross each other without restriction, as shown. In the language of non-adiabatic theory, such PESs are *diabatic*. Upon including spin-orbit coupling in the Hamiltonian, the different spin states can mix, leading to *adiabatic* PESs that do not cross (neglecting conical intersections), shown as dotted lines in Figure 1. Because of the mixing, the same adiabatic surface may correspond to different spin states in different regions of phase space. Where the diabatic surfaces cross, the corresponding adiabatic surfaces will show an *avoided crossing*, which may lead to a barrier on the lowest adiabatic PES. It is important to note that for spin-forbidden processes, the PESs for individual spin states are *diabatic*, and do not correspond to the eigenstates of the full Hamiltonian.

To return now to the semi-classical model of non-adiabatic behavior, one can describe reactions on the spin-state (diabatic) PESs as follows: The system will move throughout phase space on the reactant PES until it reaches a point where the product PES has the same energy as the reactant one. At that point, it may either remain on the reactant PES or hop over onto the product one. The Landau-Zeener formula for curve crossing in one-dimensional systems has often been used in a multi-dimensional context [10] as a useful approximation for the probability p with which this hop occurs, leaving $(1 - p)$ of the trajectories to continue on the initial PES (Figure 1).

$$p_{LZ} = 1 - \exp\left(\frac{-4\pi^2 H_{rp}^2}{h v \Delta F}\right)$$

(H_{rp} is the magnitude of the coupling between the reactant and product surfaces at that point, v is the speed of the system upon passing the point where the PESs cross, and ΔF the magnitude of the difference between the slopes on the two surfaces.) It can be seen that as the coupling becomes large, the exponential becomes small, so that the hopping probability approaches 1. This constitutes the *adiabatic* limit,‡ meaning that the system will remain on the same adiabatic PES throughout (as discussed above, this will involve a change of spin!). In the opposite limit, where H_{rp} goes to zero, the hopping probability is zero too, leading to the *diabatic* limit: the system keeps the same spin throughout, even though this involves changing from one adiabatic PES to another. Spin-orbit coupling in transition metal atoms can be very large, especially for elements of the second and third transition row, and this often applies to compounds containing the metals as well, so that in many cases, spin-forbidden processes may in fact occur in the adiabatic limit. In other cases, the electronic structure may lead to the coupling between spin states being much weaker than suggested by the atomic coupling constants, leading instead to *non-adiabatic* behavior, corresponding to a hopping probability somewhere between 0 and 1.

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‡ The use of the term *adiabatic* can be understood here by considering the effect of the v (speed) term. As the speed goes to zero, the exponential goes to zero whatever the strength of the coupling. Thus, a system moving infinitely slowly upon approaching the crossing between the diabatic surfaces will be guaranteed to behave adiabatically, that is, to remain on the same adiabatic PES. This is analogous to thermodynamic systems, which behave adiabatically when changes to parameters such as pressure or volume are introduced infinitely slowly.

This model leads to a very natural distinction between two factors influencing reactivity in spin-forbidden systems: the electronic and nuclear factors. The first of these is the strength of the coupling between the spin states. If it is very weak, a spin-forbidden process can be very slow however favorable the nuclear factor. When spin-forbidden processes are discussed with the focus on this first factor alone, the conclusion is often that the large spin-orbit coupling typical of transition-metal systems will rule out reactions involving spin changes being slow. This is in fact not the case, mainly because the nuclear factor is often more important than the strength of the coupling in determining the speed of spin-forbidden reactions. This second factor refers to the amount of energy needed to move the nuclei from the reactant minimum to the region where the two spin-state PESs cross, and is analogous to the activation energy for adiabatic reactions. If the geometries of the different spin states are sufficiently different, this energy can be quite large, and the reaction leading from one spin state to the other can be very slow, even if the electronic coupling is so strong that one is effectively at the adiabatic limit. So whatever the electronic factor, it is usually the nuclear factor which has the largest effect on the speed of spin-forbidden reactions, and computational work therefore revolves around locating the regions where the relevant PESs cross.[§]

It should be pointed out that whilst the semi-classical model is qualitatively correct, one needs also to include the possibility that the system will *tunnel* from one diabatic surface to the other. This is a manifestation of the quantum nature of the nuclei, which cannot be said to be precisely localized in phase space, but are instead smeared out in the vicinity of the classical "position". This means that the system does not quite need to reach the crossing region to hop from one spin-state PES to the other, but may instead tunnel across. To use a classically based analogy, this involves changing from one electronic state to the other, whilst simultaneously and instantly changing the nuclear configuration also. Because nuclei are heavy, the smearing of their positions is limited. In practice, this therefore means that tunneling can only occur in the vicinity of the region where the PESs cross, so that the semi-classical model whereby the spin change occurs at the crossing point is not badly wrong.

The above discussion has been very general, and much of it applies to other types of non-adiabatic process. By far the most important of these is electron transfer (ET). This involves a transition from one diabatic state to another, with each state corresponding to a different charge distribution:

$$D—A \rightarrow D^{+}—A^{-}$$

Where D and A are donor and acceptor molecules (or functional groups within a same molecule). In some cases, the two (diabatic) states can be very strongly coupled (*e.g.* in inner-sphere ET), in which case the lowest adiabatic PES will be directly accessible by *ab initio* calculations, and will have a transition state as a signature of the avoided crossing of the two diabatic states. This TS may then be localized using standard *ab initio* methods. In many other cases, however, the coupling will be weak, so that even if both

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[§] When spin-orbit coupling is *very* strong, individual spin-state PESs are quite different from the adiabatic PESs, and may not provide even a qualitatively useful zero-th order representation of the system. This is however unusual, although one can expect that in systems with strong coupling, the avoided crossing between spin state PESs may be quite strong, so that the highest point on the lower state is substantially lower in energy than the corresponding diabatic state at that point.

diabatic states have the same spin and space symmetry, they will mix only weakly in the crossing region. Similar models to those used for spin-forbidden processes can describe the behavior of such systems, a point which has been made in several theoretical contributions [9,11].

The parallel can be extended to the methods used for *ab initio* calculations on electron-transfer. Strictly speaking, the lowest *ab initio* adiabatic PES for an electron-transfer system has a TS where the diabatic surfaces cross (unless the two diabatic states have different spin or symmetry). However, the weak mixing of the diabatic states in the crossing region will lead to numerical instabilities, so that it is often impossible to locate the TS. It is then easier to study the crossing region using *ab initio* methods which "decouple" the diabatic surfaces. One way to do this relies on the fact that D interacts only weakly with A, and involves calculating PESs for D, D^+, A and A^- separately. The "reactant" diabatic PES is then given as the sum of the D and A PESs, the "product" PES as the sum of the D^+ and A^- PESs. These decoupled PESs no longer interact at all, like spin-state PESs in the study of spin-forbidden processes, and the crossing region can therefore be studied using the same techniques. Although this approach has not yet been applied in studies of ET in transition-metal systems, it has yielded very useful results for a broad range of processes, such as self exchange in O_2^- / O_2 [12] and NH_2OH^+ / NH_2OH [13], and for models of electron transfer within the photosynthetic reaction center [14].

As suggested by the above discussion of ET with strong coupling, even processes that occur adiabatically on a single *ab initio* PES can often be discussed usefully in terms of the crossing of two diabatic surfaces. This is the insight at the heart of the curve-crossing model [15] of organic reactivity. The approach can also be of practical use in computational work. Thus, most molecular mechanics force fields are unable to describe chemical reactions because the reactants and products have different bonding patterns, corresponding to different expressions for the PESs, which do not smoothly merge in the TS region. This suggests that the two expressions be treated as diabatic surfaces, and that one then search for the crossing region between these PESs, which should provide a good approximation to the TS. This approach has been shown to be reasonably successful by comparison to *ab initio* calculations [16].

In conclusion, the theory of non-adiabatic processes suggests that the key to predicting spin-forbidden reactivity in transition-metal systems is the ability to predict the properties of the region where the corresponding spin-state PESs cross. This does not mean that one assumes the occurrence of non-adiabatic behavior (although this is possible), but simply reflects the fact that the system often needs a considerable amount of energy to reach the crossing region. As discussed below, the PESs actually cross at many different nuclear configurations; the chemically significant ones will be those of lowest energy, and it is these that computational chemists need to locate.

Spin-Forbidden Chemistry in Transition-Metal Systems

In this section, I will try to illustrate the role of spin-forbidden reactions in the chemistry of transition metals. The section is intended to give some idea of the *breadth* of this chemistry; doing justice to the depth would be impossible.

Surely the longest-established type of spin-forbidden process in transition metal chemistry is the

phenomenon known as *spin crossover* [17,18]. As mentioned in the Introduction, unligated metal atoms and ions have high-spin states, with ligands tending to stabilize lower-spin states through the ligand field. It is well known that the strength of the latter can be modulated by careful choice of the ligands, so that is easy to imagine that for the proper choice of metal and ligands, the high-spin and low-spin states may be formally isoenergetic. In practice, the different states will have different optimal geometries, so that systems having such a finely balanced ligand field are able to have distinct minima corresponding to the spin states, and these can be separately observed. Because the difference in geometry can be rather small, the corresponding PESs can cross at low energies, leading to facile interconversion of the spin-states [19]. In some cases, it has also been proven that the reactivity is dominated by tunneling behavior at low temperature [20].

A important development in this field has been the discovery for some spin-crossover systems that the more stable of the two spin states can be converted to the higher state by irradiation with visible light, a phenomenon referred to as light-induced excited spin state trapping (LIESST) [21]. The reverse transformation can be induced with light of a different color, which has led to intense interest in the possibility of using such systems as light-addressable information-storage devices. Obviously, this depends on the *thermal* rate of interconversion being low, and the design of systems having this property is dependent on having a full understanding of the nuclear factor of the corresponding spin-forbidden process. Spin crossover has also been observed for many bioinorganic systems [22].

Much of the theoretical work in this field has focused on the use of empirical potentials for the two minima, and good results have been obtained [23,24]. This can be expected, because the minima corresponding to the different spin states are generally rather close, and they are well approximated by harmonic expansion of the surfaces around the minima. However, *ab initio* computations can be expected to contribute positively to this field if they are able to characterize the crossing of the PESs in a less *ad hoc* manner.

Ligand association and dissociation are more typical "reactions", in that they involve a change in the coordination sphere of the metal atom. This leads to changes in the ligand field, and so may also be accompanied by a change in spin state. The CO dissociation reactions mentioned in the introduction are good examples of such processes. Many other dissociation/association reactions have been suggested or observed to occur with a change in spin. Thus, phosphine exchange in singlet $CpCo(PPh_3)_2$ was suggested to occur *via* a triplet intermediate, $CpCo(PPh_3)$ [25]. This has been investigated in a recent computational study which has shown that the related $CpCo(PH_3)$ complex does indeed have a triplet ground state, with the singlet lying considerably higher in energy [26].

For this reaction, spin-forbidden ligand dissociation should be *faster* in this system than the spin-allowed process, providing the crossing region is energetically accessible, and that spin-orbit coupling is not too small. For systems having similar low-spin to *low*-spin dissociation energies, reactions such as this one which have a lower-energy *high*-spin dissociation channel will be faster than reactions where the intermediate has a low-spin ground state. This idea, whereby spin-forbidden reactions can turn out to be *faster* than related spin-allowed ones has received considerable experimental and computational attention [27]. This was prompted by the observation of facile ligand exchange in the doublet $CpMoCl_2(PR_3)_2$

complexes, which was suggested to occur *via* quartet $CpMoCl_2(PR_3)$ intermediates [28]. Whilst these have been shown to indeed have quartet ground states [27], the details of the crossing behavior have only recently [29] been established using one of the methods presented here, and these results will be discussed in a later section. Given the basic role of ligand dissociation and association reactions in inorganic and organometallic chemistry, computational contributions to understanding the role of spin-state changes are especially desirable.

The ligand association reactions of CO and O_2 with haem in its quintet state to form singlet haem-CO or haem-O_2 (Figure 2) are bioinorganic spin-forbidden processes of tremendous importance. The relevance of the spin-forbidden nature of these reactions became significant very early on, and extensive theoretical as well as experimental work has been performed on these reactions [30,31,32]. It would be of great importance to explore the relevant PESs and ascertain whether surface crossings lead to effective barriers for these reactions.

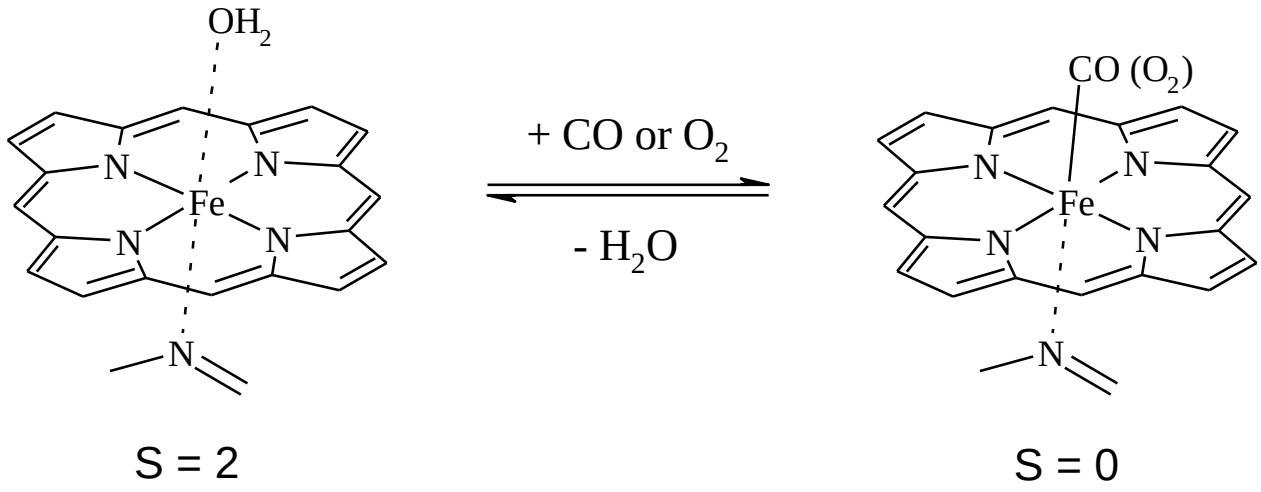


Figure 2. Spin-forbidden addition of singlet CO or triplet O_2 to quintet haem to form singlet carbonyl-haem or oxy-haem.

Oxidative addition is really only a more complicated form of ligand association, and also leads to large changes in the coordination properties of the metallic center which is involved. It is therefore not surprising that this process, as well as its reverse, reductive elimination, also involve changes in spin in many cases. Such addition processes, when they involve C–H bonds, are key steps in the catalytic functionalization of alkanes and have received considerable experimental attention due to their potential industrial importance [33]. CpIrCO and CpRhCO have been found to insert efficiently into the C–H bond of methane, whereas the first transition-metal row congener, CpCoCO does not [33,34]. Computational studies have shown that the iridium and rhodium compounds have singlet ground states, or very low excitation energies to singlet states, whereas the cobalt compound is a triplet, meaning that a crossing must occur *en route* to the inserted $CpCoH(CO)(CH_3)$ species [34]. In the same paper, it was estimated that this crossing would occur at relatively high energies, and the difficulty of locating the crossing region more accurately was discussed at length.

Ultrafast kinetic studies have been performed on the insertion of photolytically generated singlet and

triplet $CpM(CO)_2$ (M=Re,Mn) intermediates into the Si–H bond of the $(C_2H_5)_3SiH$ molecule. The rhenium compound is a singlet, whereas the manganese derivative is primarily a triplet under the experimental conditions, and this has been shown to affect the kinetics of the two processes [35].

Oxidation chemistry is a general term covering a range of processes, many of which include metal oxides. Because of the small spatial extent of metal-centered *d* orbitals, spin pairing in multiply-bonded oxo species is rather weak, leading to similar energies for the low spin M=O and high spin •M–O• configurations, which have completely different reactivities. Given this fact, it is not surprising that spin-forbidden processes are particularly common in this field, as has been evidenced by both experimental and computational studies. Organic synthesis requires new selective oxidation methods, so that lots of examples of spin-forbidden reactions come from this field, such as the epoxidation of alkenes by manganese-based catalysts [36] or the oxidation chemistry of chromyl chloride CrO_2Cl_2 [37,38]. Studies of bioinorganic oxidation chemistry has also highlighted the occurrence of many spin-forbidden reactions, *e.g.* in the manganese-based photosynthetic oxygen evolution in Photosystem II [39], or the oxidation chemistry of cytochrome P-450 *via* iron-oxo species [40].

Gas phase chemistry has extensively explored the effect of spin on reactivity in transition metal chemistry, largely thanks to the unrivalled possibility to perform state-specific chemistry. Gas-phase chemistry of *neutrals* has by and large mostly addressed the chemistry of small molecular species such as $Fe(CO)_5$ [41] and derivatives thereof. The spin-forbidden recombination of CO with the product of $Fe(CO)_5$ photodissociation, $Fe(CO)_4$, has already been mentioned [2]. Many other similar reactions have been studied, *e.g.* the association reactions of $Fe(CO)_4$ with other ligands, such as H_2, C_2H_4, N_2 [42,43], and the reactions of substituted derivatives such as $Fe(CO)_3(C_2H_4)$, which are also assumed to be triplets [44]. Whilst most of these reactions are observed to be slower than the gas collisional rate, not all of them are, and the substitution effects have been discussed in some detail [42]. Such discussion would undoubtedly be clarified by an accurate characterization of the PESs and of their crossings using *ab initio* methods. In turn, this is likely to provide valuable insight that can be transposed to mechanisms in condensed phase systems.

Considerable work has already been carried out on using *ab initio* calculations to predict the photodissociation dynamics of gas-phase metal carbonyls [45]. This is a fertile area for computational work, given the extensive experimental results available, which include the use of ultrafast methods to characterize the short time behavior in photoexcited states. There is considerable evidence that surface crossings, especially of a spin-forbidden nature, play a considerable part in the dynamics. Much of the theoretical work so far has focused on reduced-dimensionality models of the PESs, which have been used in quantum-mechanical studies of the non-adiabatic nuclear dynamics, in which spin-forbidden transitions are frequently observed [45]. Here, too, the potential benefits to be derived from a proper understanding of the spin-state chemistry are considerable, due to the importance of light-induced processes in organometallic and bioinorganic systems.

Mass spectrometric investigation of "bare" metal ions and of their reactions with small molecules has also contributed enormously to the understanding of transition-metal chemistry. It might seem that bare metal ions, as well as ions bearing a few ligands only, are not representative of typical catalysts due

to their extensive coordinative insaturation. However, it has been observed many times that they do in fact display remarkably similar reactivity patterns to the condensed-phase analogues [46], and they therefore provide excellent models for study, especially in terms of the level of experimental detail which is accessible. It should also be stated that the limited molecular size of such models lends itself to achieving much higher levels of computational accuracy than is currently possible with larger molecular arrays.

This field of investigation has accordingly grown considerably in the last years, and only a few highlights can be mentioned here. State-selected reaction rates have been measured for reactions with various hydrocarbons, clearly demonstrating the higher reactivity of low-spin states [47]. This work has also been extended recently to reactions of neutral metal atoms [48,49]. Trends have been established by studying *identical* reactions for the whole ten elements of a given transition metal period, which is completely impossible for condensed phase compounds [50,51]. In many cases, these periodic comparisons have shown that spin has an important effect on thermochemistry and kinetics of transition metal compounds. The intricate electronic structure of metal-oxo species has been examined and related to the extreme complexity of the reactivity of such compounds [52]. The chemistry of the iron oxide cation, FeO^+, has received considerable attention, with a particular focus on the spin-forbidden steps which occur during oxidation by this species [53,54]. This work on the gas-phase FeO^+ ion has led to valuable insight into the role of spin in the bioinorganic oxidation chemistry of cytochrome P-450, already mentioned above [40].

Spin-forbidden processes are extremely common in transition metal chemistry. Both experimentalists and computational chemists are increasingly confronted by this fact, creating a need for useful models of how spin changes influence reactivity. Computational chemistry should play a key role in developing such models, using the methods discussed in the next section.

Computational Study of PES Crossing

As already indicated in the Theory section, the computational chemist needs to locate the regions of configurational space where PESs cross so as to be able to understand, rationalize, and provide useful predictions for all of the fascinating chemistry discussed in the previous section. More precisely, he or she must locate the regions of lowest energy where crossing occurs.

Construction of Global PESs

As in computational studies of adiabatic processes, for systems having more than three or four atoms, it is not at all realistic to compute the PESs completely and systematically. However, one such study has been performed for the $Sc^+ + H_2$ system, within the side-on C_{2V} approach mode, and 2D PESs have been constructed as a function of the H–H and Sc–H_2 midpoint distances, using calculations at the MR-CISD level of theory [55]. This seminal study is important because it explicitly considered the implication of the PESs for the kinetics and dynamics of the spin-forbidden insertion reaction:

$$Sc^+ (^3D) + H_2 \longrightarrow ScH_2^+ (^1A_1)$$

Thus, all the triplet surfaces were found to be mainly repulsive, because triplet Scandium (^{3}D, [Ar]3d^{1}4s^1), with its two parallel valence electrons, cannot form bonds to both hydrogen atoms. However, the $^1A_1$ state is found to cross one of the triplet states near the singlet transition state for dissociation into Sc^+ (^{1}D). The authors point out that this crossing region is accessible for moderately energetic Sc^+ (^{3}D) and H_2 reagents, allowing the spin-forbidden reaction to occur by surface hopping [55].

Although similar studies are impossible for more realistic systems, the general topology of the PESs involved in spin-forbidden ligand recombination and oxidative addition reactions is often rather similar to that obtained for ScH_2^+. High-spin PESs tend to be repulsive, due to the impossibility of forming bonds with the incoming ligands, whereas at least one of the low-spin PESs is attractive at least in parts, and the two tend to cross in the entrance channel. The details of the PESs and of their crossing region determine where the crossing occurs, and so the kinetics of the reaction. Because of the generality of this picture, the paper by Rappé and Upton [55] has been of great use to experimental and computational chemists investigating similar spin-forbidden processes, especially those involving small gas-phase ions.

It should be noted that it is of course possible to construct complete PESs even for polyatomic systems, if one only treats a limited number of degrees of freedom. One can thus perform *ab initio* calculations on a grid of points generated by varying only a few structural parameters. This method has been used in the context of quantum dynamical studies of photodissociation in metal carbonyl derivatives [45]. The study of $HCo(CO)_4$ dissociation, for example, was performed on PESs which only considered the Co–H and Co–C_{axial} bond lengths, the other parameters being frozen [56]. This approach is certainly useful, but like other approaches discussed below, by completely neglecting relaxation of the frozen geometrical parameters, it will not always be very accurate

Qualitative Evaluation of Crossing Profiles

Qualitative information on the crossing behavior of spin-state PESs is frequently enough to give a good idea of the likely importance of the nuclear factor on the kinetics of a spin-forbidden process. For example, if the minima of two spin states are rather similar in geometry, as well as lying close in energy, one can fairly reliably predict that they will cross at fairly low energies. Additional information can be derived from considering the force constants for motion towards the other minimum.

In fact, such approaches can be used for assessing *adiabatic* reactivity also: two structurally similar minima are likely to be connected by a relatively low-lying transition state, especially if the force constants corresponding to motion towards the other minimum are small. In practice, with the development of efficient gradient-based methods for optimizing transition states [57,58], and their general availability, such qualitative reasoning is rarely employed, except for trivial transition states, *e.g.* for rotation around single bonds.

For spin-forbidden reactions, because the better methodologies are less available at present, many studies have in fact relied on the inspection of surfaces. It is to be stressed that this may often be quite satisfactory when qualitative considerations alone are of interest. To take an example, Fe^+ has a ^{6}D ground

state, which is unreactive with alkanes in the gas-phase. The low-lying excited ^{4}F state is able to insert into C–H bonds. Computational studies of the gas-phase reactions of Fe^+ with methane [59] and ethane [60] have shown that the quartet and sextet complexes between the metal ion and the alkane lie close in energy. The sextet energy rises well above the quartet as the system then moves towards the relatively high-lying quartet C–H or C–C insertion TS. In such cases, it is reasonable to suppose that the system is able to reach the PES crossing region at relatively low energies, so that interconversion of the spin states will occur rapidly compared to the insertion. According to the Curtin-Hammett principle [61], this means that the spin-forbiddenness of the insertion will not affect its kinetics.

Computing single point energies on one PES at the minima, TSs or other important points on the other PES leads to a refined understanding of the nature of the surface crossing. This is due to the fact that PESs can be assumed to be relatively smooth, which narrows down the energy range where crossing can be expected to occur. This is illustrated in Figure 3, where the position of the PES corresponding to the spin state of the products (bold line) is shown at several critical points on the PES of the reactant spin state (solid line). It can be seen that a reasonable estimate of the crossing position can be obtained, providing the product PES does not have the unexpected shape shown by the dotted line.

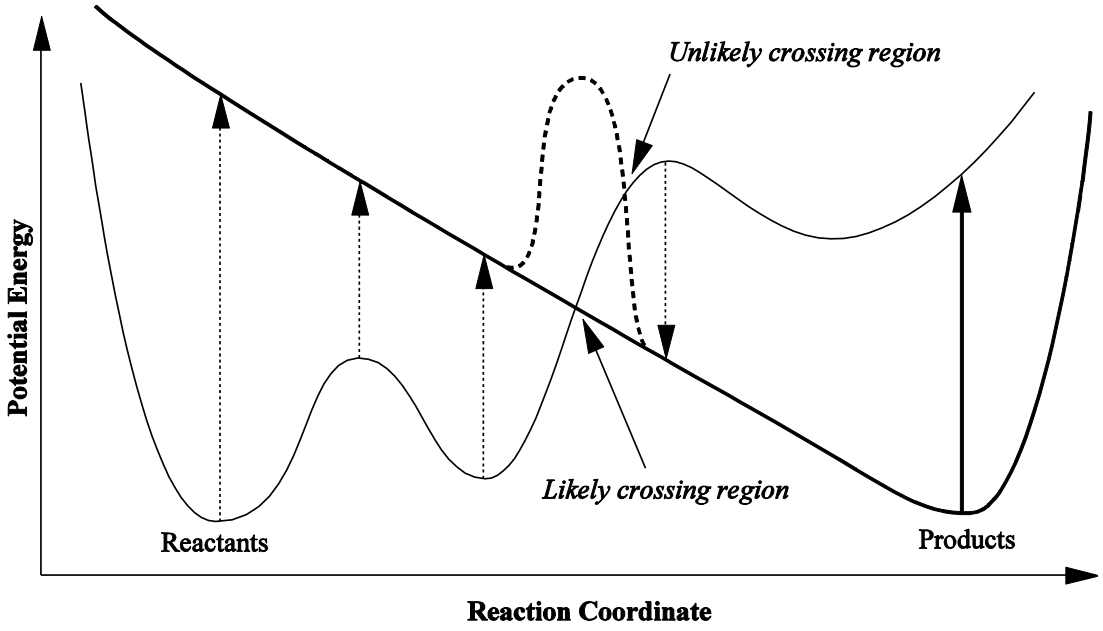


Figure 3. Schematic representation of a spin-forbidden reaction, showing how knowledge of the energy on one PES at selected points on the other PES can lead to reasonable assumptions as to the location of a surface crossing. For these assumptions to be wrong, unexpected behavior of one or both of the PESs, as shown by the bold dotted line, is necessary.

An even more refined approach involves computing the energy on one PES at a whole range of geometries on the other PES, *e.g.* along an optimized IRC. This approach has been used to characterize PES crossings in the $FeO^+ + CH_4$ system [62], as well as in the model system for chromyl chloride oxidation of alkenes, $CrO_2Cl_2 + C_2H_4$ [37]. This procedure gives some insight as to where the crossing between PESs occurs along a reaction coordinate.

Overall, such qualitative approaches for characterizing the crossing region between two PESs can be extremely useful, especially in cases where the exact details of where the crossing occurs are not expected to affect the kinetics of a reaction. Quantitative accuracy, however, is unfortunately impossible. This should be obvious for the simpler approaches discussed above. However, upon performing *ab initio* studies on multiple PESs of different spin, there is a tendency to plot the results together on a single diagram, giving potential energy as a function of a single "reaction coordinate". This leads to something resembling Figure 3. However, at most points, the vertical difference in energy between the lines representing different PESs on such a Figure will be meaningless. At best, when single points have been computed on one PES at optimized points on the other PES, one knows the energy at a few points on both surfaces simultaneously. In the worst case, which is also the more common one, one knows the energy at one set of geometries on one PES, and at another set of *different* geometries on the other PES. Even when one has computed the "same" intermediate on both surfaces, the corresponding geometries will have been optimized and will frequently differ significantly. It is therefore misleading to plot such points above one another, to draw lines between them, and especially, to attribute any precise significance to where the lines cross. This completely neglects the role of differential *relaxation* on the two PESs of the multiple geometric parameters that cannot possibly be represented on the one-dimensional plot.

To conclude, it should be stressed that the objections in the previous paragraph concerning the temptation to interpret one-dimensional pictures of the crossing of PESs in a *quantitative* way are in no way aimed at discrediting qualitative approaches for characterizing surface crossings. It should simply be realized that these approaches cannot give exact energies and structures for the lowest point where two PESs cross. In cases where the crossing appears to lie just above or just below some critical energy for the system being considered, more quantitative methods are thus needed.

The Method of Partial Optimization.

One of these more systematic approaches, which has been called the method of partial optimization [29], relies on identifying a single geometrical coordinate which has very different optimal values in the two spin states. This coordinate can typically be a bond length, a bond angle, or a combination of several such coordinates. Next, a set of partial geometry optimizations are performed on each surface, whilst holding the value of the unique coordinate fixed. Repeating this operation for several values of the unique coordinate, and on both PESs, leads to two one-dimensional sections through the PESs, which, providing the coordinate has not been poorly chosen, will cross at some point. This leads to 1-dimensional graphs similar to Figures 2 or 3, and in principle allows a much more precise evaluation of the energy and geometry of the crossing region.

This approach has been used *e.g.* in studies of the recombination of CO with $Fe(CO)_4$ [63]. As mentioned above, $Fe(CO)_4$ has a triplet ground state, whereas the recombined product $Fe(CO)_5$ is a singlet. The triplet PES is essentially repulsive for all distances as the incoming ligand approaches, whereas the singlet PES is attractive throughout, so that there is a crossing, as shown schematically in Figure 4. The most natural unique coordinate to use for partial optimization in this system is the Fe–C distance of the dissociating CO ligand, and this is indeed the choice made in ref. [63].

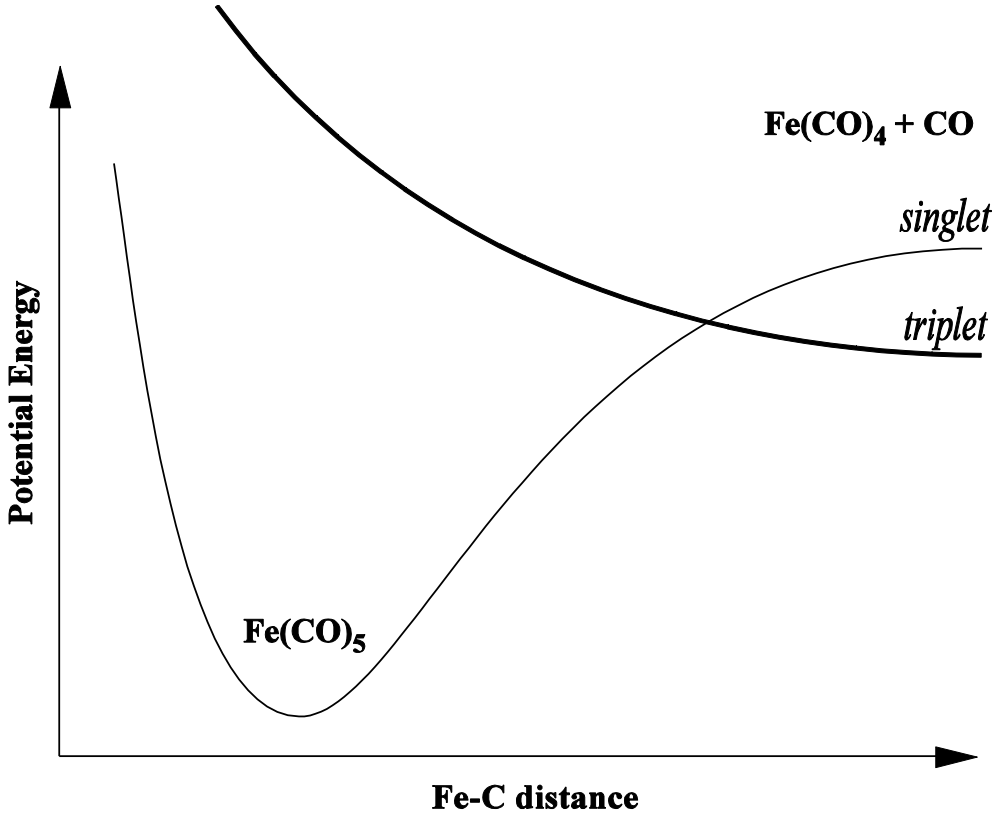


Figure 4. Schematic representation of the singlet and triplet PESs in the $Fe(CO)_4$ + CO system.

The calculations in that study were performed using the BLYP density functional, with an ECP on the iron atom, together with large triple to quadruple-zeta polarized basis sets [63]. At this level, the $^3B_2$ state of $Fe(CO)_4$ lies 3.8 kcal.mol^{-1} below the $^1A_1$ state. The authors did not give precise details concerning the location of the crossing point, but on their graph showing the partial optimization curves, the crossing can be seen to occur for r(Fe–C) between 3.5 and 4.0 Å, and at an energy which is almost the same as that of singlet $Fe(CO)_4$ + CO. This suggests that the nuclear factor is quite substantial in this reaction, with a considerable barrier to recombination being formed. It appears that this barrier occurs because the singlet PES is not yet significantly attractive at the Fe–C distances where the triplet PES is already rather repulsive. The crossing behavior in this system will be discussed at greater length in the next section.

An advantage of the partial optimization method is that it leads to the location of a refined "crossing" point compared to the mere qualitative consideration of the PESs. It also provides appealing one-dimensional plots of the potential, apparently giving considerable insight into the mechanism, *e.g.* as to the "early" or "late" nature of the crossing with respect to the two minima. However, the approach does not lead to quantitative results, for much the same reasons as discussed above. The crossing "point" that is found is in fact *two* points, lying on the projections of the two PESs onto two *different* one-dimensional sections of configurational space. This is because the curves describe the energies of the two states at *separately optimized* configurations on the two PESs, with only the unique coordinate guaranteed to be equal. If the other coordinates have very different equilibrium values on the two PESs along the curves, as can be expected given the differences in electronic structure, one will need to climb in energy from

both sides to reach configurations that are the same for each spin state. The energy of the "crossing point" is only a rough lower estimate of the energy of the lowest point where the multidimensional PESs really cross. Of course, careful selection of the unique coordinate may somewhat alleviate this problem, but it cannot be completely eliminated.

The main disadvantage of the partial optimization method is that it is rather computationally expensive, since it requires multiple geometry optimizations on both PESs. The method discussed below is not only more accurate, but it also requires only the equivalent of one geometry optimization on each surface, so it should really be preferred in most cases when the qualitative approaches of the previous section are not suitable.

Explicit Optimization of the Minimum on the Crossing Seam

The above methods for characterizing the regions where different PESs cross are intrinsically approximate, even though they may often yield information of sufficient accuracy for the individual case being studied. As noted, some of them can also turn out to be of considerable computational expense. When an accurate result is desired, it is actually possible to locate directly and exactly the point of lowest energy where two PESs of different spin cross. Locating the minimum energy crossing point (MECP), as it is often called, can be done in the same way that one finds minima or transition states on single PESs, by geometry optimization using energy gradients. Methods for finding MECPs have been described by several groups [64–71], with all relying in essence on minimizing a generalized gradient derived from the energies and gradients on the two PESs. The version used in much of the work described here is based on the following gradient, $\vec{g}$ [65]:

$$\vec{g} = \alpha(V_1 - V_2)(\vec{g}_1 - \vec{g}_2) + \vec{g}_1 - \vec{h}(\vec{g}_1 \cdot \vec{h})$$

(Where α is an arbitrary constant, V_1 and V_2 are the potentials on the two PESs, $\vec{g}_1$ and $\vec{g}_2$ the corresponding gradients, and $\vec{h}$ a unit vector parallel to $(\vec{g}_1 - \vec{g}_2)$). The minimization is performed with the BFGS approximate second order method [72], and the whole optimization is driven by a shell script which calls the *ab initio* program to generate V_i and $\vec{g}_i$, extracts them from the output, and uses them to update the geometry until convergence is reached.[**] The advantage of this script method, which has been used before [68], is that it can very easily be adapted for use with a variety of *ab initio* program packages. The version used here can be obtained upon request from the author.

Several features of the method are worthy of note. First, the (local) minimum on the crossing seam is fully optimized. As well as providing the energy, this provides a considerable amount of *structural* information, including of course the most favorable geometry for spin change. This can be of considerable use in understanding reaction mechanisms, by examining the deformations the system undergoes with respect to the minimum. Thus, bond stretching or shortening can be related to bond-breaking or formation, or to changes in bond order, changes in angles can be related to changes in hybridization, etc. Also, the gradients on the two PESs are parallel at the MECP, and they thus jointly

[**] With a reasonable starting geometry, speed of convergence is similar to that obtained for minima.

define one unique direction, which is analogous to the transition vector of adiabatic reactions, providing a clue to the orientation of the reaction coordinate at the MECP. A more detailed reaction coordinate can be obtained by optimizing two "reaction paths", steepest descent paths from the MECP on the two PESs. Also, it is possible to check that the MECP is indeed a minimum within the seam of crossing between the PESs, and not a saddle-point, by computing and diagonalizing a generalized Hessian [70] in the same way as one computes frequencies at an adiabatic stationary point.

Second, there exist simple methods, analogous to transition state theory, for predicting rates of spin-forbidden reactions, based on the properties of the MECP [71,73,74]. Whilst these have not yet been applied to systems containing transition metals, they could of course be useful for exploring to what extent the *electronic* factor plays a role in such cases.

Third, the method involves a *single* geometry optimization, using information at each point from the two surfaces, and should thus be roughly as computationally demanding as one geometry optimization on each PES. In many cases, this should be much less than for the partial optimization method - as well as leading to a better accuracy.

Finally, it is possible to use a hybrid low/high level approach [70] to locate MECPs, which can be useful when analytical gradients are unavailable at the level of theory needed to describe the two PESs and their relative energy correctly. Of course, it is essentially meaningless to perform single-point calculations at a high level at the geometry of an MECP optimized at a lower level, because there is no guarantee that the PESs will have the same energy at the higher level. However, one can use the lower level to optimize the geometry, under the constraint that the *higher-level* energies are equal [70]. This relies on the fact that the lower level should reproduce the features of the PES *orthogonal* to the reaction path reasonably accurately, even if it completely fails to describe the relative energies of the two PESs. This principle is also the basis of the IRCMax method [75] for accurately determining adiabatic barrier heights using high-level energies and low-level gradients.

The MECP optimization technique has, as yet, been used for only a handful of transition metal systems. I will hereby discuss a few of these studies, so as to provide insight into how the method compares with the other approaches discussed above. The gas-phase reactions of Sc^+ with small molecules such as H_2O [76] and CH_4 [77] are relatively simple examples of spin-forbidden reactions which will serve as a good introduction. As mentioned above, Sc^+ has a ^3D ($[Ar]3d^14s^1$) ground state with a low-lying singlet excited state. The triplet is unable to insert into the X–H bonds of H_2O or CH_4, because it cannot form two new bonds, whereas the singlet can, leading to relatively stable closed-shell intermediates $H–Sc^+–XH_n$.

The Sc^+ / H_2O system has been the object of a number of computational studies [78,79,80], which have all located the key stationary points on the singlet and triplet PESs. These include the singlet and triplet $Sc^+–OH_2$ ion molecule complexes, the insertion transition state leading to $H–Sc^+–OH$, the H_2 elimination TS, and the resulting $ScO^+–H_2$ ion-molecule complex; the latter three points all having singlet ground states. The most recent paper [80] uses B3LYP density functional calculations, with DZVP basis sets, together with CCSD(T) single point calculations with TZV basis sets and multiple polarization

functions. The authors loosely discuss the effect of spin on this reaction, and claim that the singlet PES crosses below the triplet one somewhere between the reactant ion-molecule complexes and the inserted $HScOH^+$, at an energy below that of the separated reagents, Sc^+ and H_2O. This is based on the fact that the triplet reactant complex is more stable than the singlet, whereas the inserted product has a singlet ground state, with the corresponding triplet lying substantially in energy. The inserted species are very different in nature, since $^1HScOH^+$ is a well-characterized molecule with two metal-element bonds, whereas "inserted" triplet $HScOH^+$ is in fact better described as a very loose complex between $ScOH^+$ ($^2\Delta$) and an H atom, and has a very long Sc–H "bond".

The singlet and triplet energies along the reaction profile are thus derived from *separately* optimized and significantly different geometries, so that qualitative reasoning cannot be used to determine the crossing energy accurately, as discussed in previous sections. This is especially important because the crossing is estimated to occur close to the TS for O–H bond insertion on the singlet PES, and that this TS lies only slightly lower in energy than the reactants, $Sc^+ + H_2O$ [80]. Under thermal conditions, the reaction would be unlikely to occur if the crossing occurs somewhat higher than the reactants' energy, and this cannot really be excluded on the basis of qualitative estimates of the crossing energy.

To clarify this issue, new B3LYP calculations, using the Gaussian 98 program suite [81] together with our script for optimization of MECPs [71], have been performed to investigate the crossing behavior more closely [76]. A similar basis set to that of reference [80], *i.e.* the SVP basis set [82], augmented by an *f* polarization function on Sc, diffuse *s* functions on H, and diffuse *s* and *p* functions on O, has been used. As expected, similar results to those described in previous studies are obtained for the stationary points (Figure 5):

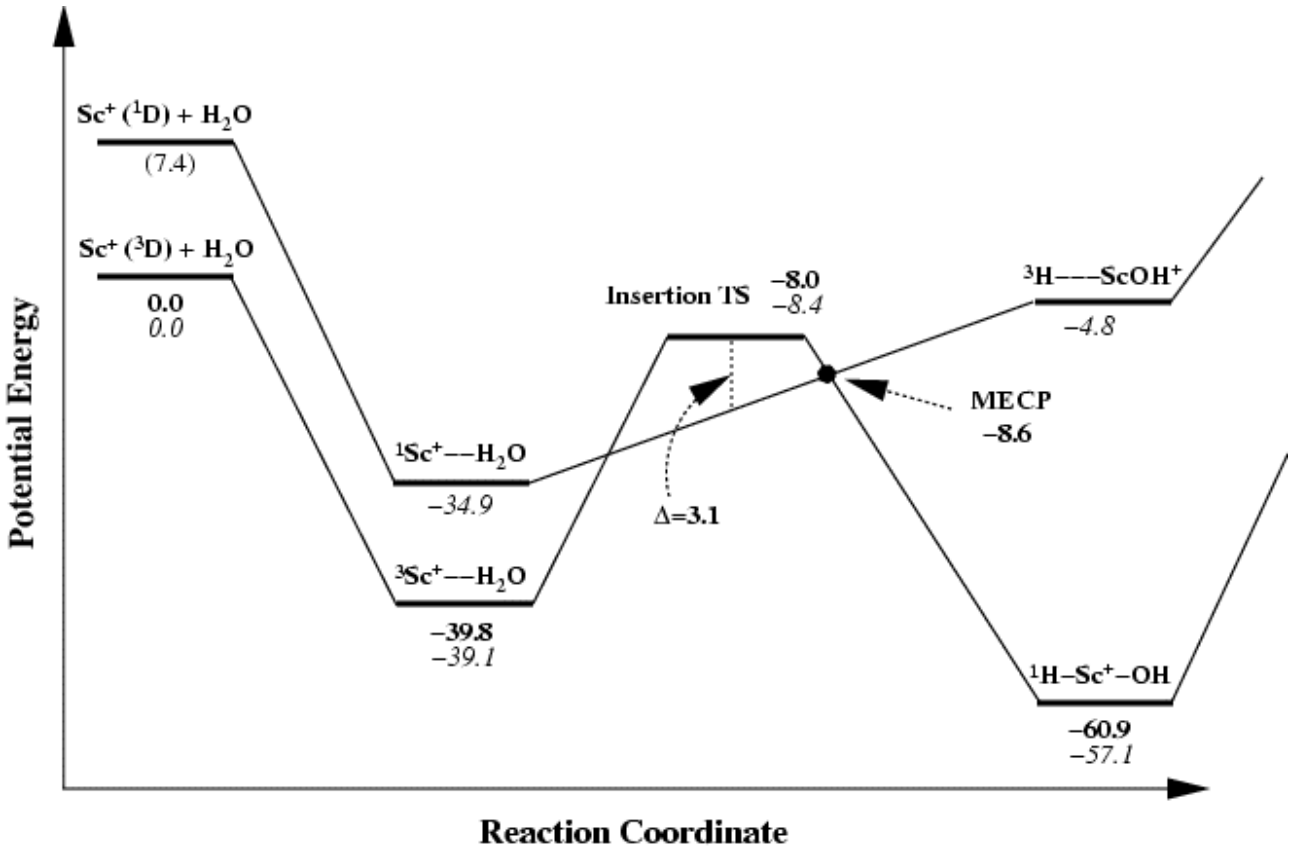


Figure 5. PESs in the $Sc^+ + H_2O$ system. Energies are in kcal.mol^{-1} relative to reactants, with the numbers in bold taken from ref. [83], and the numbers in italics from ref. [80]. The excitation energy of Sc^+ is the experimental value (see ref. [80]).

The new result is the optimization of the MECP between the ^{1}A' and ^{3}A' PESs. This point is indeed found to lie lower in energy than the $Sc^+ + H_2O$ reactants, and very close, both in geometry and in energy, to the TS. As can be seen in Figure 5, the triplet state still lies somewhat lower in energy than the singlet at the TS itself, however, indicating that the crossing occurs "after" the TS. This is further confirmed by the fact that following the gradient downhill from the MECP on the singlet surface leads directly to the inserted species $HScOH^+$. It is noteworthy that the energy difference at the TS is sufficiently small to make it relatively obvious that the MECP occurs at low energies, using the qualitative reasoning discussed above. However, the explicit optimization of the MECP provides completely unambiguous proof that it does indeed lie at an energy which is thermally accessible, and thereby that the reaction should be fairly fast unless spin-orbit coupling is very small.

The corresponding reaction with methane has PESs that are rather similar to those described here, so that it will not be discussed in detail. It should however be pointed out that the description of the MECP in this system appears to have been one of the first such reports for a transition metal system in the literature [77]. The study used CASSCF calculations with four electrons in an eight-orbital active space, combined with polarized double zeta basis sets [77]. Dynamical correlation is not very important in this system, partly because Sc^+ only has one d electron, so that this level of theory produces rather good agreement with experiment for quantities such as the ^{1}D ? ^{3}D excitation energy, the complexation energy of CH_4 and Sc^+, and the insertion energy to form singlet $H–Sc^+–CH_3$. It can thus be expected that the region of the surface crossing is well described, too. The authors find an MECP lying slightly lower in energy than the TS for C–H bond insertion on the singlet PES, and crossing is predicted to be facile in this system too, in agreement with experiment.

The second example, the association reaction of CO with triplet $Fe(CO)_4$ to form singlet $Fe(CO)_5$ [2], has been discussed in previous sections. A partial optimization study of the crossing behavior in these systems has been performed [63], leading to the conclusion that crossing occurs at long Fe–C distances, where the singlet PES is not yet attractive, but is not repulsive either, and the triplet state is repulsive. A substantial barrier to association was predicted, in poor agreement with experiment. To examine the accuracy of the partial optimization method, new calculations [83] have been performed to locate the MECP explicitly, using the BLYP and B3LYP density functionals as implemented in Gaussian 98 [81], together with the SVP basis set [82]. A schematic representation of the optimized structure of the C_{2v}-symmetric MECP is shown in Figure 6, and geometric parameters of the MECP and various minima together with relative energies are presented in Table 1.

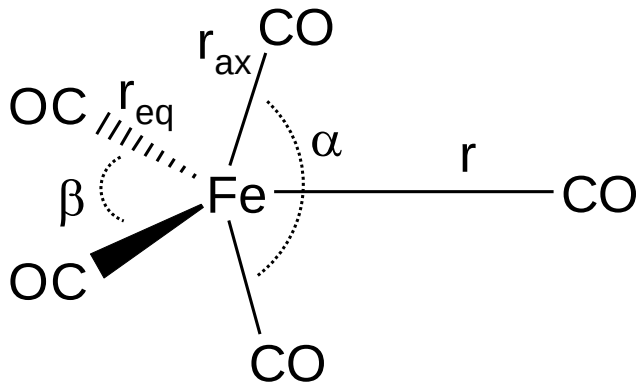


Figure 6. Structure of the MECP between the lowest singlet and triplet PESs of $Fe(CO)_5$, with a definition of the structural parameters referred to in Table 1.

Table 1. Geometric parameters (Å, degrees) and relative energies ($kcal.mol^{-1}$) in the $Fe(CO)_5$ system, taken from ref. [83]. The molecules belong to the following point groups: $Fe(CO)_5$: D_{3h}; singlet and triplet $Fe(CO)_4$ and MECP: C_{2v}; except for singlet $Fe(CO)_4$ at the BLYP level: D_{2d}.

		r	r_{ax}	r_{eq}	α	β	E_{rel}
B3LYP	$Fe(CO)_5$ ($^1A_1'$)	1.813	1.822	1.813	180.0	120.0	-33.3
	$Fe(CO)_4$ ($^3B_2$)	/	1.875	1.847	146.9	98.9	0.0
	$Fe(CO)_4$ ($^1A_1$)	/	1.821	1.784	154.5	128.7	9.1
	MECP	2.557	1.901	1.843	165.8	102.3	5.2
BLYP	$Fe(CO)_5$ ($^1A_1'$)	1.825	1.827	1.825	180.0	120.0	-42.1
	$Fe(CO)_4$ ($^3B_2$)	/	1.868	1.831	147.3	98.8	0.0
	$Fe(CO)_4$ ($^1A_1$)	/	1.806	1.806	141.0	141.0	0.5
	MECP (BLYP)	2.933	1.867	1.823	159.2	103.1	3.0

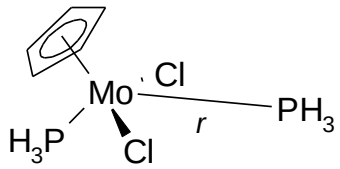
The results of this study are quite different from those obtained using the partial optimization method, which shows the importance of structure relaxation. Thus, the MECP has a much more compact structure, in terms of the dissociating Fe–C bond distance, than it does in the previous study, where *r* was between 3.5 and 4.0 Å. At the lower values of *r* predicted here, the singlet surface is already significantly bonded, so that in the case of the B3LYP method, the MECP is actually significantly *lower* in energy than the dissociated products on the singlet PES. A more striking difference with the behavior expected from partial optimization occurs for the data derived using the BLYP functional. As with other "pure" density functionals, the energy difference between the singlet and triplet states of $Fe(CO)_4$ is

predicted to be much smaller than that obtained using the B3LYP functional which partially includes HF "exact" exchange (This appears to be a general trend for pure and hybrid functionals [84,85]). Because BLYP predicts the triplet to lie only 0.5 kcal mol^{-1} below the singlet for r = 8, the partial optimization method would predict the PESs to cross at very long values of r, since the triplet surface only to rise very slightly, or the singlet surface to become slightly attractive, for the energy difference to be annihilated. However, this neglects the fact that the structures of singlet and triplet $Fe(CO)_4$ are significantly different, so both will need to be distorted so as to reach the MECP. This explains why the present calculations find the MECP to lie significantly higher than both the singlet and triplet dissociation products, and at a fairly small value of *r*. The optimized *r* is however slightly higher than that obtained at the B3LYP level, indicating that the crossing does occur somewhat "earlier" along the association pathway than in that case.

These results show that the partial optimization method can yield misleading results. In terms of the chemistry, definitive conclusions are not forthcoming, because the BLYP and B3LYP functionals do not agree as concerns the singlet-triplet energy difference of $Fe(CO)_4$, and it is not known what the exact result is. However, the disagreement concerning the barrier to recombination is less severe, with both levels predicting a barrier of 3-5 kcal.mol^{-1} with respect to triplet $Fe(CO)_4$. This will need to be tested by more extensive calculations using other density functionals or methods [83].

A final example concerns the dissociation reactions of the doublet complexes $CpMoCl_2(PR_3)_2$, which have already been mentioned. So as to definitively prove that this system is directly able to reach the quartet PES *en route* to dissociation into $CpMoCl_2(PR_3)$ and phosphine, we have undertaken a study of the crossing behavior in the $CpMoCl_2(PH_3)_2$ model system [29]. Because previous work on related systems [86] had used the partial optimization method, we compared the results derived from that method with the fully optimized MECP. The calculations [29] were performed with the B3LYP density functional, together with the standard LanL2DZ basis set, which includes effective core potentials (ECPs) to treat the innermost core electrons on Mo, Cl and P, and using the Gaussian 98 program [81]. The results are summarized in Table 2:

Table 2. Structure of the MECP in the $CpMoCl_2(PH_3)_2$ system, together with relative energies (in kcal.mol^{-1}). Adapted from ref. [29].

		r	E_{rel}
	$^2CpMoCl_2(PH_3)_2$		-8.7
	$^2CpMoCl_2(PH_3) + PH_3$		9.2
	$^4CpMoCl_2(PH_3) + PH_3$		0.0
	Partial Optimization Crossing Point	3.43 Å	2.3
	MECP	3.20 Å	4.1

In this case, the agreement between the two methods is reasonable, with both predicting the crossing to occur very slightly above the energy of the dissociated intermediates, in the quartet state. Because this energy region is well below the *doublet* dissociation energy, both methods predict that $CpMoCl_2(PR_3)_2$ complexes should be able to dissociate faster by a spin-forbidden route to quartet $CpMoCl_2(PR_3)$ than by the spin-allowed route, in agreement with the original prediction [28]. As shown in Table 2, there is also reasonable agreement concerning the geometry of the crossing, although here again, the more accurate method also predicts a more compact structure for the crossing. However, it is important to note that the partial optimization calculations in this case were considerably more expensive than the MECP optimization. The latter required about 35 energy + gradient computations on each PES (= 70 in total), compared to a total of 282 energy + gradient computations for the five partial optimizations on both surfaces.

Ab initio Methods and Crossing Points

As for all computational studies, spin-forbidden processes require a very careful selection of the electronic structure method to be applied. In the main, the choice is made in the same way. Thus, one tries to find a level of theory that is both affordable and accurate. Accuracy can be guaranteed by choosing the highest levels of *ab initio* theory, multi-reference CI with a large number of reference configurations, and a very large basis set. As always, and especially in transition metal chemistry, this is very rarely a realistic approach, and one seeks instead to calibrate a lower level of theory to the problem one is treating. This can involve simply comparing the predictions of the level chosen with available experimental data for the system. A better calibration can often be obtained by comparing a *set* of increasingly accurate computational methods with experiment. Even if the methods chosen are all cheaper than the intended

level to be used, this can give valuable information as to how well the predicted properties are converged with respect to the level of theory. Comparison with *more* accurate methods often requires performing the calibration calculations on a smaller model system, or on parts of the PESs to be studied only.

This sort of reasoning is of course available in the general literature, so that there is no need to further extend the discussion. One point which does need to be raised, however, is that the method chosen to locate an MECP needs to reproduce the energy difference between the spin states as well as possible. It frequently happens that a computational method leads to the PES of one spin state of a system being substantially higher than it should be, *e.g.* because that state has more correlation energy, and the method only obtains a small part of the correlation energy in each state. In such cases, the energy "offset" will lead to a sometimes quite serious error on the energy and geometry of the MECP. An example of this can be seen in the above calculations on the MECP in the $Fe(CO)_4$ + CO system, where the BLYP and B3LYP levels lead to different predictions for the energy difference between singlet and triplet states. This leads to different MECP geometries, and significantly different energies as well. Of course, in this case, it is not known which of the methods is correct (or least incorrect!), as mentioned above. In cases where the level of theory needed to treat the two PESs in a balanced way does not yield analytical gradients, one can use the hybrid method of ref. [65], as discussed above.

A final point of some importance concerns the use of single-reference methods. Density functional theory is often the method of choice in computational transition metal chemistry, simply because it is often the only affordable method which yields a qualitatively accurate description of the PESs. However, it is in some respects a "single-reference" method in that it constructs a "wavefunction" from a single Slater determinant, and cannot therefore describe systems that inherently require a representation in terms of multiple determinants, such as low-spin open-shell systems. This makes it inappropriate for treating some regions on PESs, although experience shows that DFT is somewhat less sensitive to this effect than other single-determinant systems.

One could argue that this makes DFT unsuitable for the location of *all* MECPs and the description of spin-state crossing regions in general. This is because the *adiabatic* wavefunctions at the MECP are inherently multi-referential in nature, since they are mixtures of diabatic states of different spin. However, MECP location *never* treats the adiabatic wavefunction - only the diabatic states. This is why finding crossing regions is such a problem for *ab initio* methods. Were spin-state-mixed *ab initio* calculations generally available, it would probably be the case that single-determinant approaches would be unsuitable. However, in the present state of affairs, this is not necessarily so. Whilst some PES crossings occur in regions where one or both of the diabatic states is inherently multi-referential (think of the H_2 molecule with $r = 8$, where singlet and triplet states "cross"), this is far from being always the case. In fact, most of the systems described here do not have this problem, and single-reference approaches are perfectly acceptable. It is therefore *not* automatically necessary to use multi-reference methods such as MCSCF to treat MECPs between spin states (although it is again stressed that *some* systems *will* need such a treatment). In fact, MCSCF may frequently fail the test of giving a balanced treatment of different spin states, given the fact that it often does not recover a large proportion of the dynamical correlation in a system. In such cases, MCSCF will actually be a very bad electronic structure method to use for examining

MECPs!

Conclusions

In this Chapter, I have tried to give a feeling for the importance of spin-forbidden processes in transition-metal chemistry. This is certainly relevant to much of inorganic and organometallic chemistry, to catalysis, and to bioinorganic chemistry. I have also described how understanding such processes is a challenge for computational chemists. This is because it requires the simultaneous consideration of multiple PESs, even in cases where spin-orbit coupling is so strong that the reaction can be considered to occur adiabatically on a single PES which changes smoothly from one spin state to the other. This is because the Hamiltonian used in *ab initio* calculations does not include spin-orbit coupling, and so can only calculate *diabatic* PESs having a definite spin.

I have also shown that a number of rather simple methods can be used to characterize the crossing behavior in such systems. Which is the most appropriate of these methods depends on what one wishes to find out about the system. However, for cases where the most accurate information possible is desired about the crossing behavior, the explicit optimization of the MECP is recommended in preference to the partial optimization, due to its less ambiguous conclusions and lower computational expense. Overall, the flowchart in Figure 7 can be used to design a computational investigation of a spin-forbidden process:

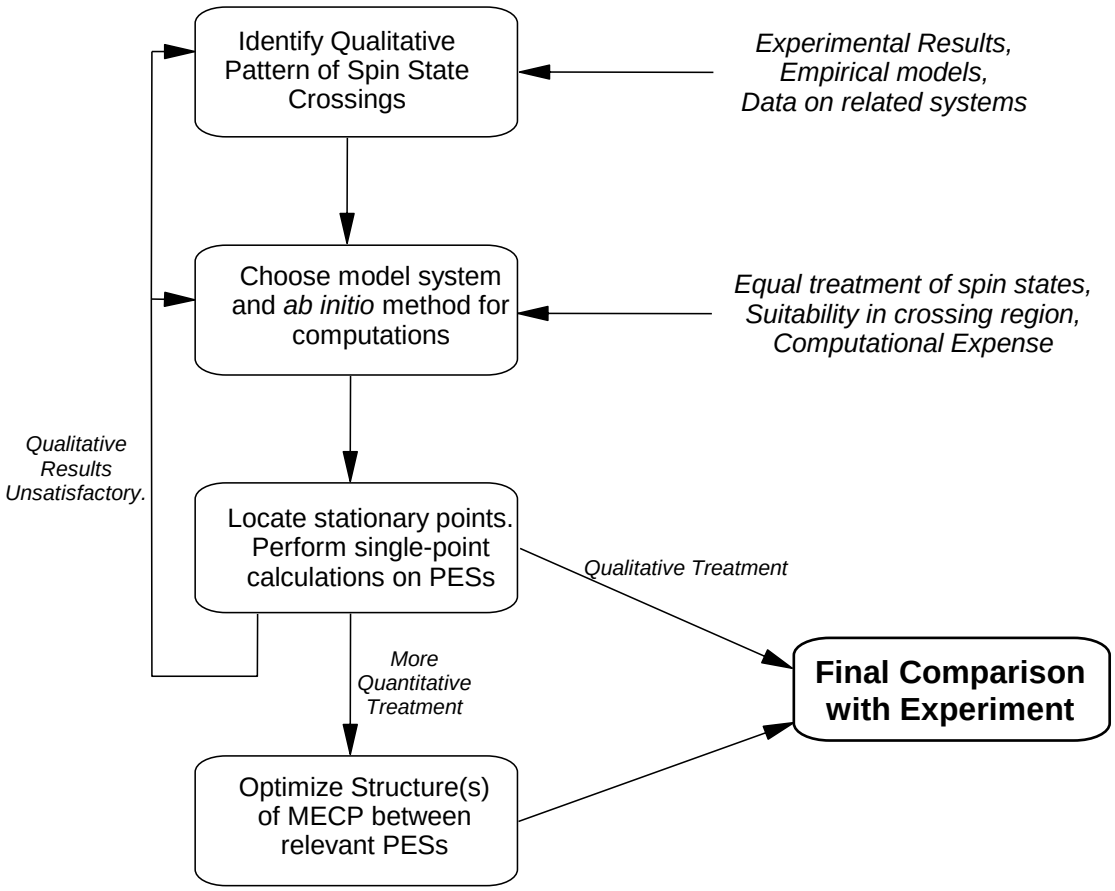


Figure 7. Flowchart for planning a computational study of a spin-forbidden reaction.

In this chart, the starting point is the identification of any possible spin-forbidden behavior, based on experimental results or on empirical models of likely spin-pairing in the reagents, products, and hypothetical intermediates. In some cases, this may already allow one to exclude the significant occurrence of spin changes during the reaction to be investigated. It also enables the design of an appropriate model for the *ab initio* investigation. Great care should be taken at this stage to ensure that the chosen model and computational method will give a reasonably accurate description of the relative energetics of different spin states. After locating the minima and transition states that are present in the initial reaction scheme, one can compute single point energies on other PESs at these optimized geometries. In some cases, this may lead to sufficiently useful qualitative understanding of the spin-forbidden behavior, and no further work is then needed.

However, in other cases, the initial calculations may lead to a re-evaluation of the whole reaction scheme, and possibly to the consideration of supplementary spin states. Less drastically, it may lead to a change in which atoms of the real system are included in the model, or to the use of a different computational method should the initial one prove too inaccurate or too computationally demanding.

As a final step, if quantitative information is required about the crossing behavior, the structure of MECPs relevant to the mechanism should be optimized. When analytical gradients are unavailable at the level of theory required to provide a reliable description of the relative energies of the different PESs, the hybrid method can be used to optimize the MECP.

Overall, one can certainly expect that the coming years will see a growing number of contributions addressing the role of spin in transition metal chemistry. It is hoped that the present overview will provide useful insights into the challenges implicit in *ab initio* computational studies of spin-forbidden processes, and will to some degree assist in attaining a higher degree of predictive power in such work.

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